



# Refractory carbides for hydrogen erosion resistance in carbon tubes for nuclear thermal propulsion

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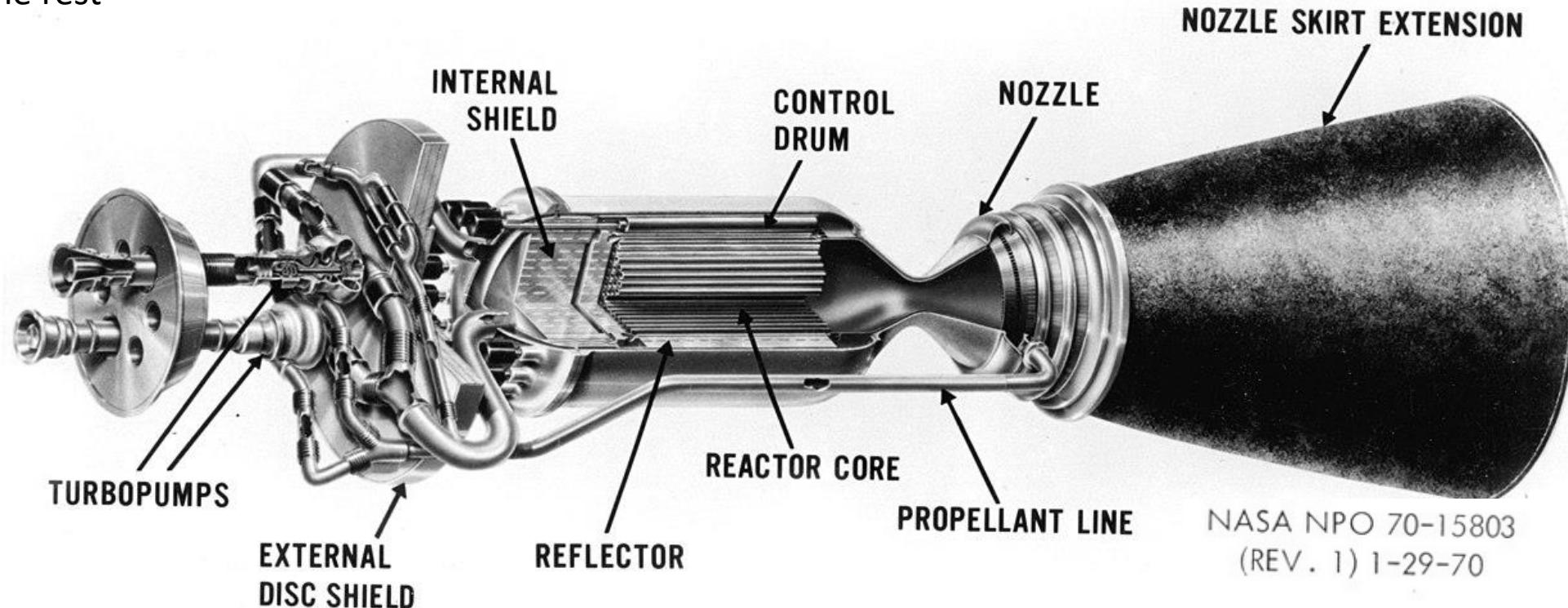
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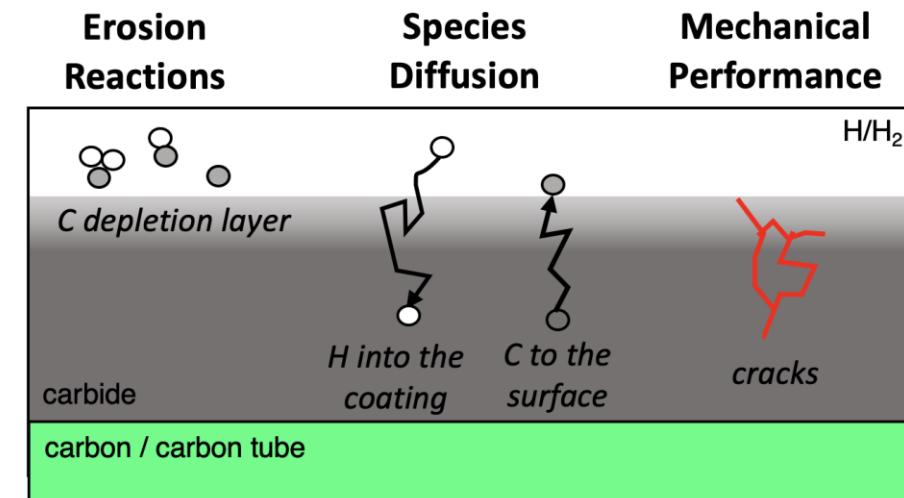
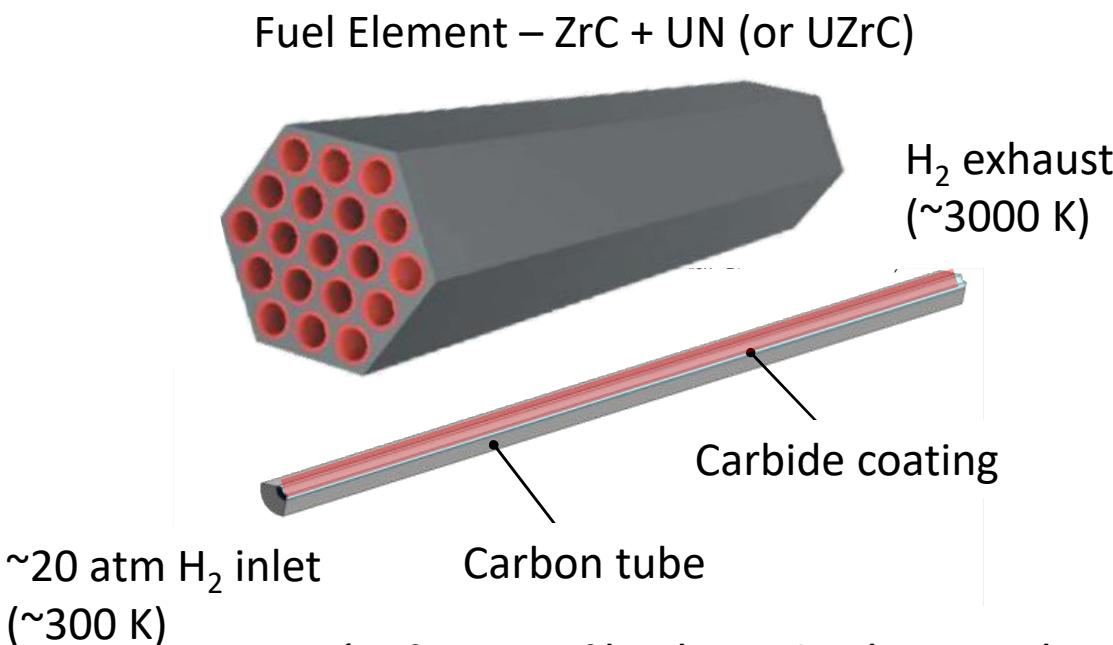
# Background

- Space Nuclear Propulsion (SNP) is an enabling technology for crewed travel to Mars
  - Nuclear Thermal Propulsion (NTP) or a Chemical/Nuclear Electric Propulsion (NEP) hybrid setup
  - In NTP, cryogenically stored H<sub>2</sub> propellant passes from tanks through a turbo, is used to cool the exhaust thruster, then passes through another turbo stage and finally enters the cold end of the nuclear core. After heating to a few thousand degrees, the hydrogen is allowed to exhaust via the thruster and conservation of momentum does the rest



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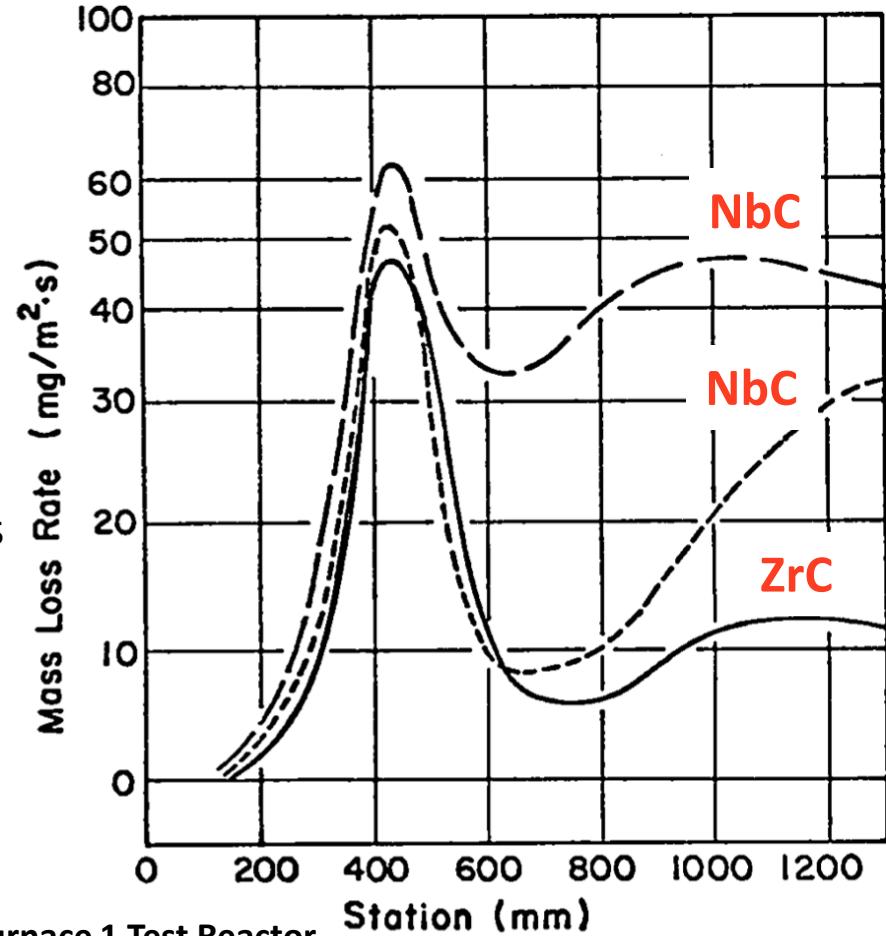
*Illustration of relevant carbide-hydrogen interactions speculated from Lyon<sup>1</sup>*

<sup>1</sup>Performance of (U,Zr)C-Graphite (Composite) and of (U,Zr)C (Carbide) Fuel Elements in the Nuclear Furnace 1 Test Reactor 3

# Background/Motivation



- Carbide coatings used to protect carbon tubes from hydrogen attack (low diffusion/erosion)
- Outcomes of carbide coated tube performance from NERVA<sup>1</sup>:
  - Mid-range erosion noted in cooler regions due to CTE mismatch
  - Mass loss suspected to be driven by carbon loss through the coating
  - Role of carbon loss on hydrogen migration through the coating not clear
  - Other studies<sup>2</sup> show that single carbides are unsuitable for various reasons
  - Neutronic considerations exclude Hf, probably Ta as well
  - End goal is probably solid solution Nb/Zr carbide – but at what ratio and carbon depletion level?
  - Methods: mostly Density Functional Theory simulations, other techniques as needed



<sup>1</sup>Performance of (U,Zr)C-Graphite (Composite) and of (U,Zr)C (Carbide) Fuel Elements in the Nuclear Furnace 1 Test Reactor  
L. Lyon. LA-5398-MS. LANL, 1973; <https://www.osti.gov/biblio/4419566>

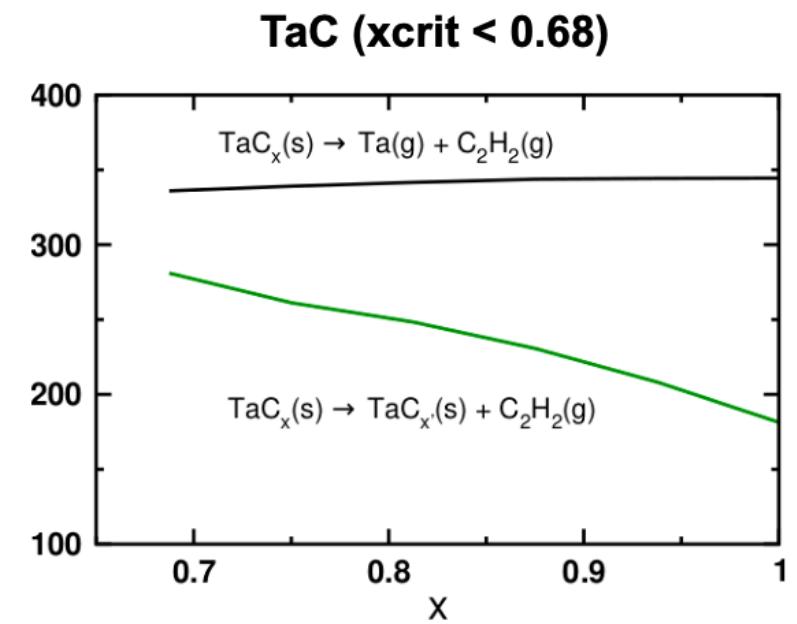
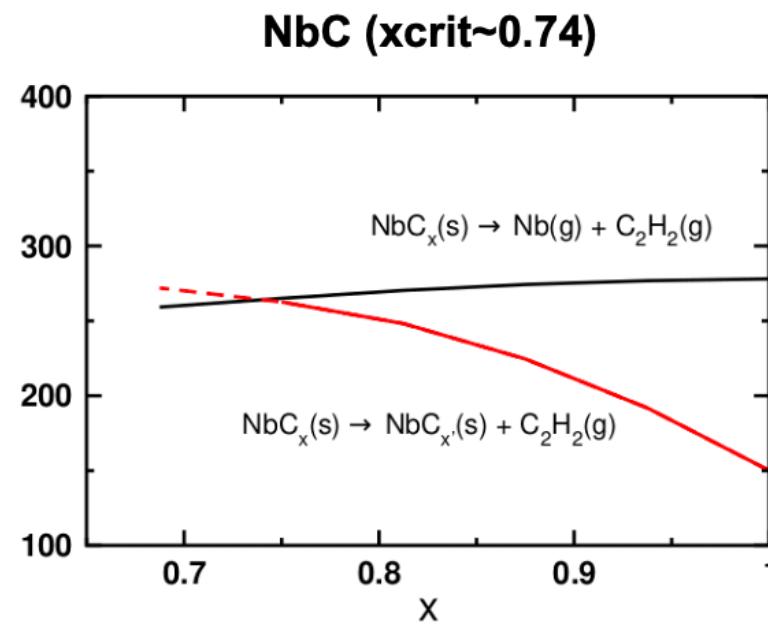
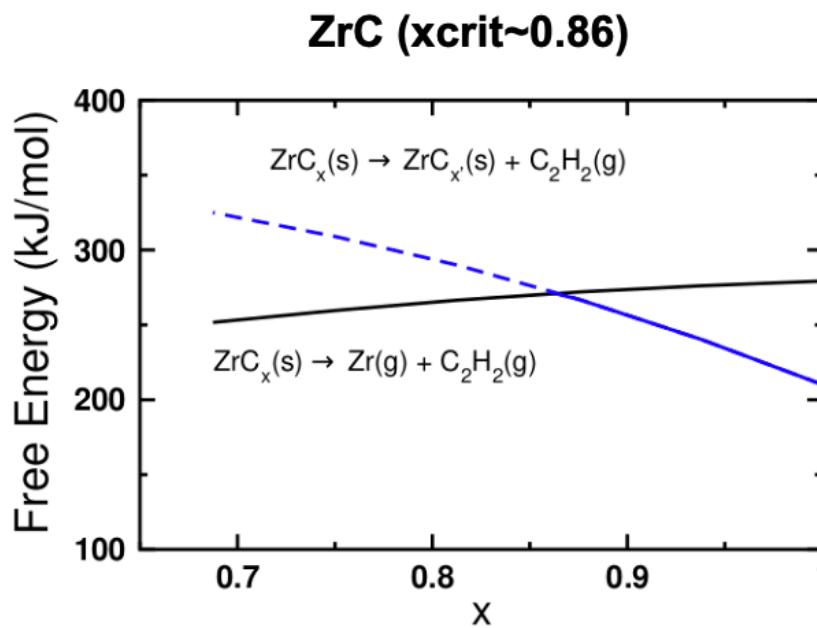
<sup>2</sup>Comparison of carbide coatings for graphite based fuel elements  
L. Cadoff. WANL-TME-1275. Westinghouse, Astronuclear Lab, 1965; <https://www.osti.gov/biblio/4174466>



# Carbon Depletion Effects

- Carbides can become carbon deficient at the surface through hydrogen reactions up to a critical carbon to metal ratio ( $x$ )
- ZrC shows best resistance to preferential carbon loss

Carbon Hydrogen Reaction (2100K)

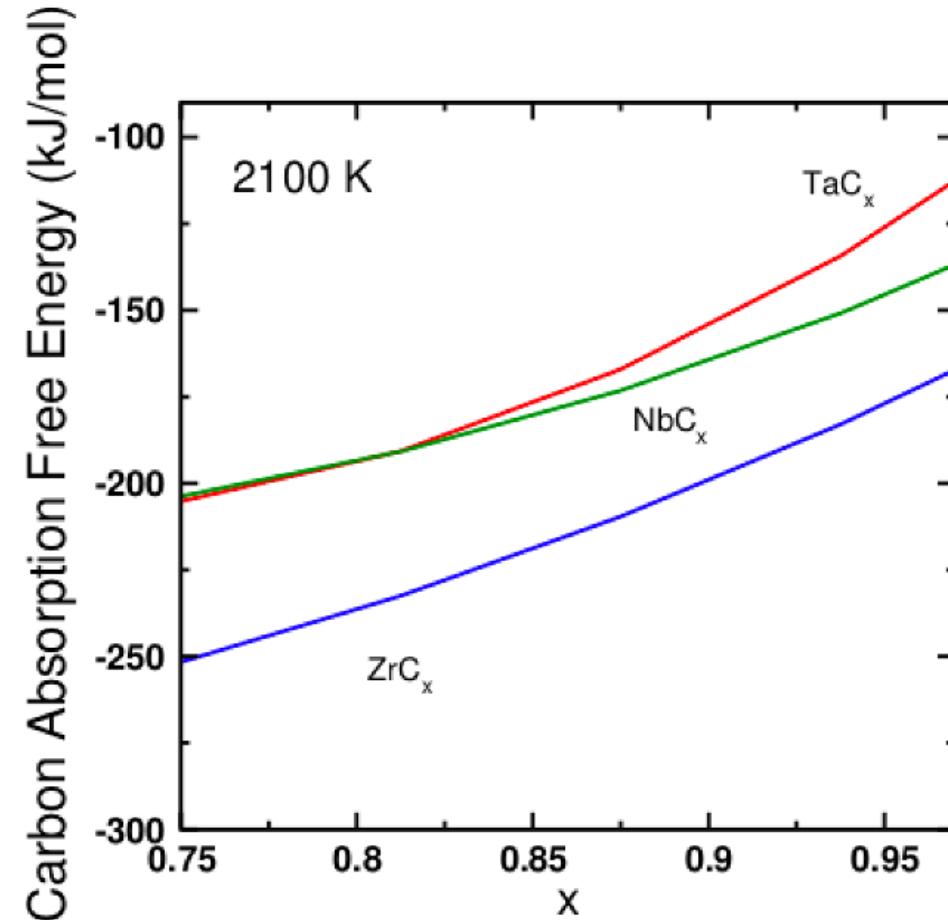


# Carbon Uptake



- Carbon lost from the carbide surface can be readily taken from solid carbon (e.g., C/C tubes)
- Free energy of filling vacancies in depleted carbides shows they all readily accept carbon

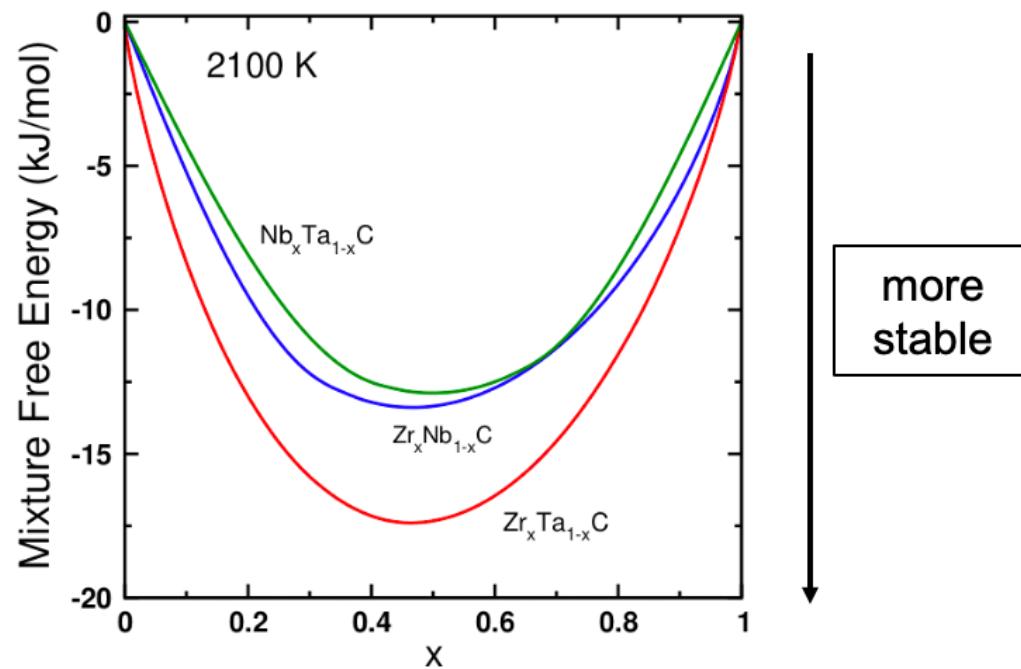
Carbon Uptake from Carbon/Carbon



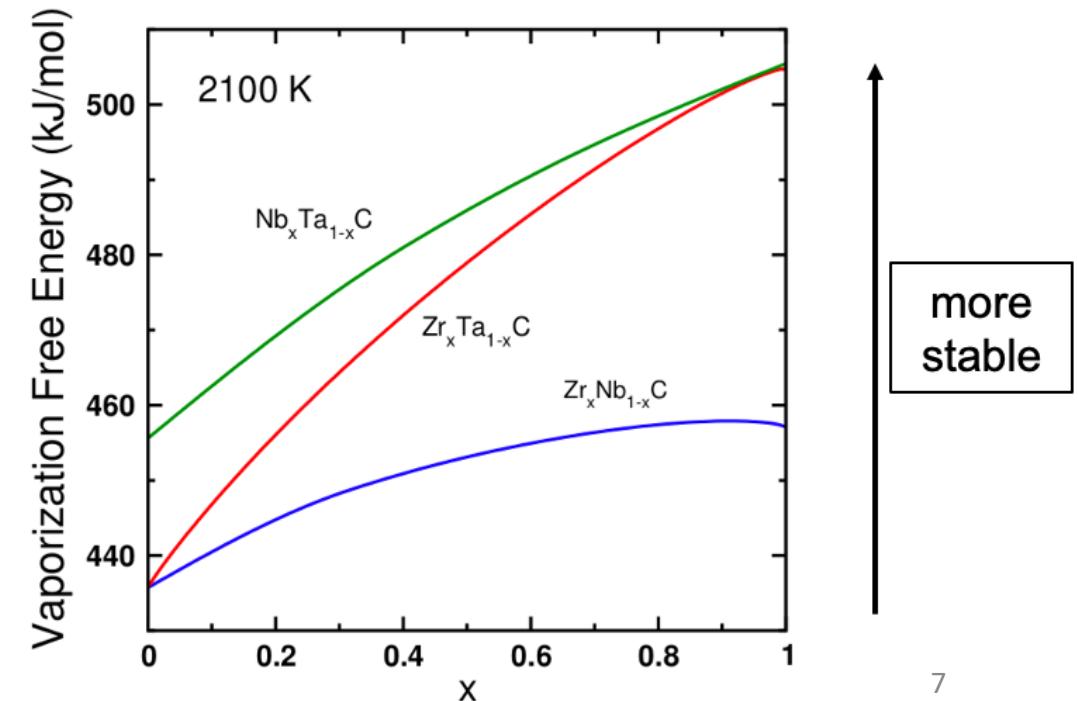
# Mixing Effects

- Mixing carbides has a large, nonlinear influence on stability and free energetics
  - Internal database developed for  $Zr_xNb_{1-x}C$ ,  $Zr_xTa_{1-x}C$ , and  $Nb_xTa_{1-x}C$  ( $T=298-3500\text{ K}$  and  $x=0.0-1.0$ )

Mixing carbides into binaries results in a chemical stabilization as demonstrated by the mixture free energy



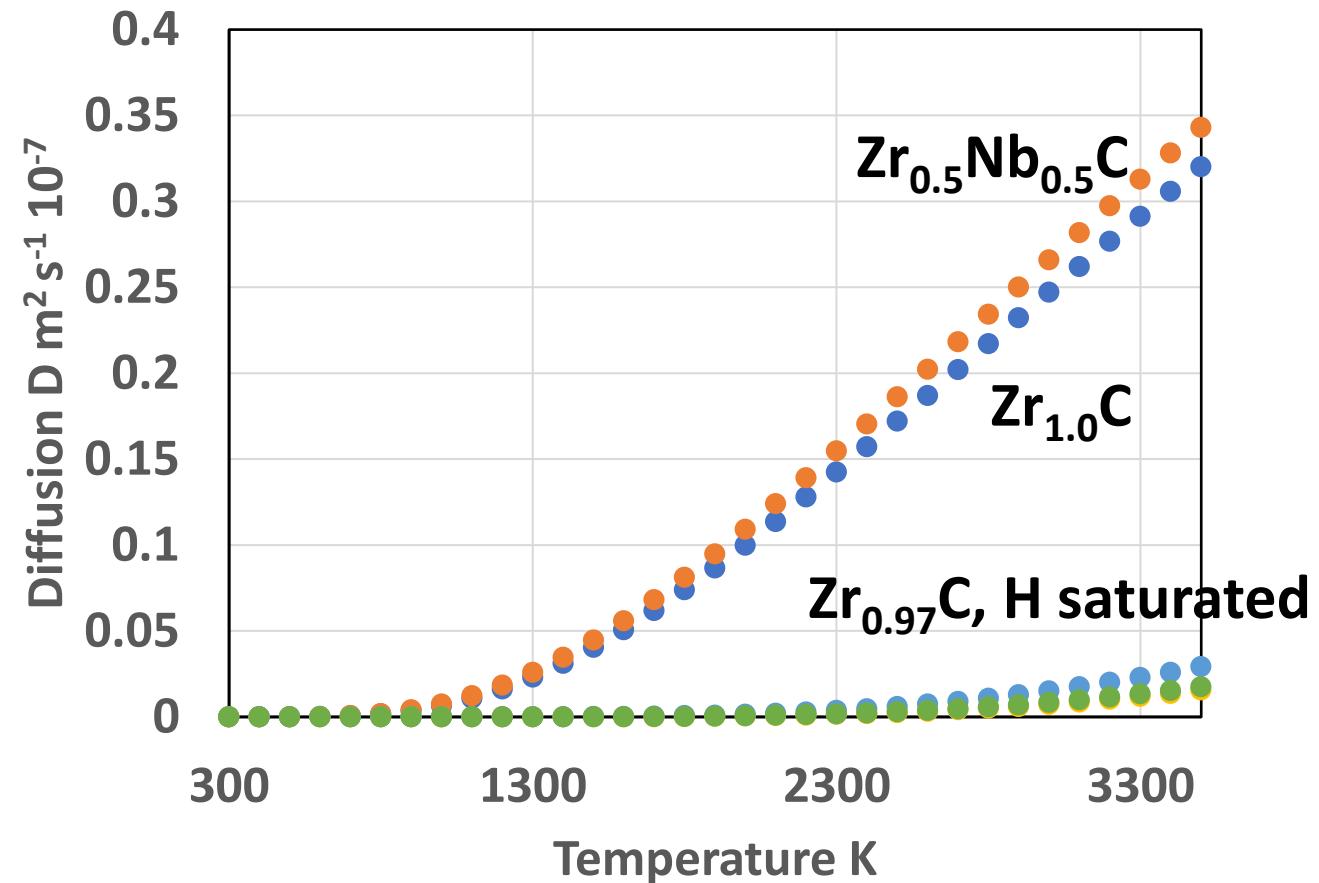
Non-linear vaporization behavior of mixed carbides as demonstrated by the vaporization free energy



# ZrC & ZrNbC: Hydrogen diffusion



- Hydrogen diffusion in carbides
  - Transition state theory
  - ZrC H diffusion slightly higher than predicted by others<sup>1</sup>
  - ZrNbC H diffusion slightly higher than ZrC
  - In substoichiometric ZrC, saturation of vacancies with H slows diffusion through bulk by ~10x

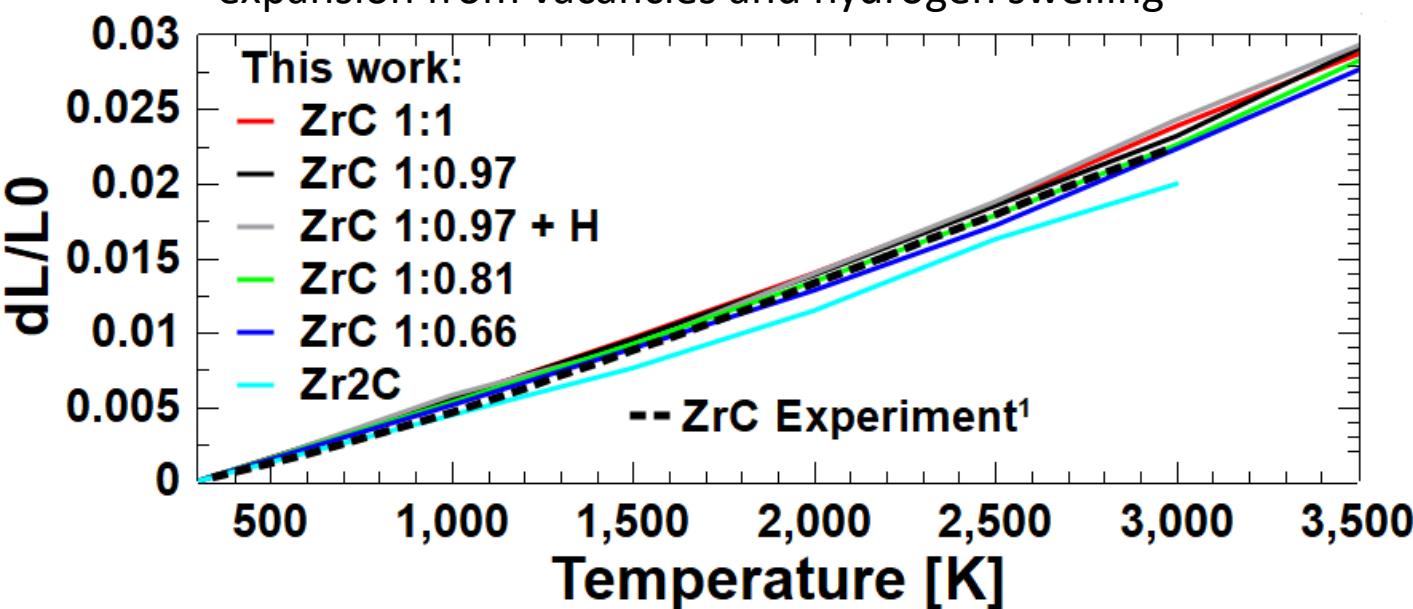


<sup>1</sup>Wang et al., The structure stability, diffusion behavior and elastic properties of stoichiometric ZrC bulk with interstitial hydrogen defect: A first-principles study. 2019. <https://doi.org/10.1016/j.jnucmat.2019.04.041>

# Mechanical Properties - DFT



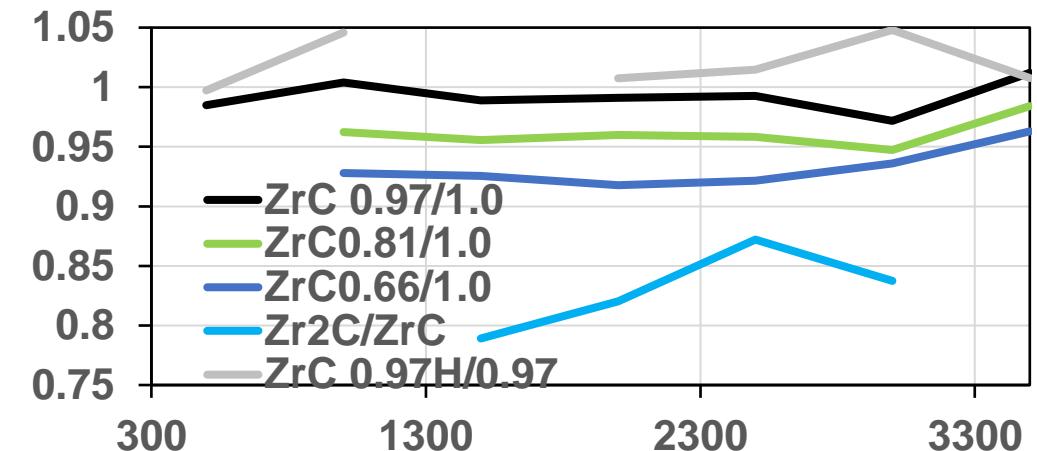
- High temperature thermal expansion of carbides
  - Experimental values compare favorably with a mixture of stoichiometries for ZrC
  - ZrC ratio plot to right shows presence of vacancies lead to reduced thermal expansion, and hydrogen causes slight swelling
  - ZrNbC ratio plot below again shows reduced thermal expansion from vacancies and hydrogen swelling



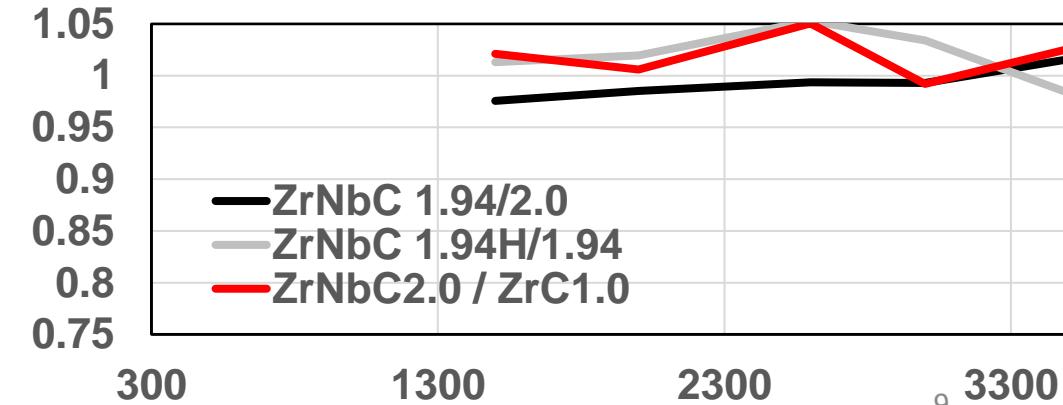
<sup>1</sup>Y.S. Touloukian, C.Y. Ho, Thermophysical Properties of Selected Aerospace Materials.,

Thermophysical Properties of Seven Materials, Thermophysical and Electronic Properties Information Analysis Center, Lafayette, IN, 1977

Ratio of thermal expansion to Zr:C  
1:1 stoichiometry

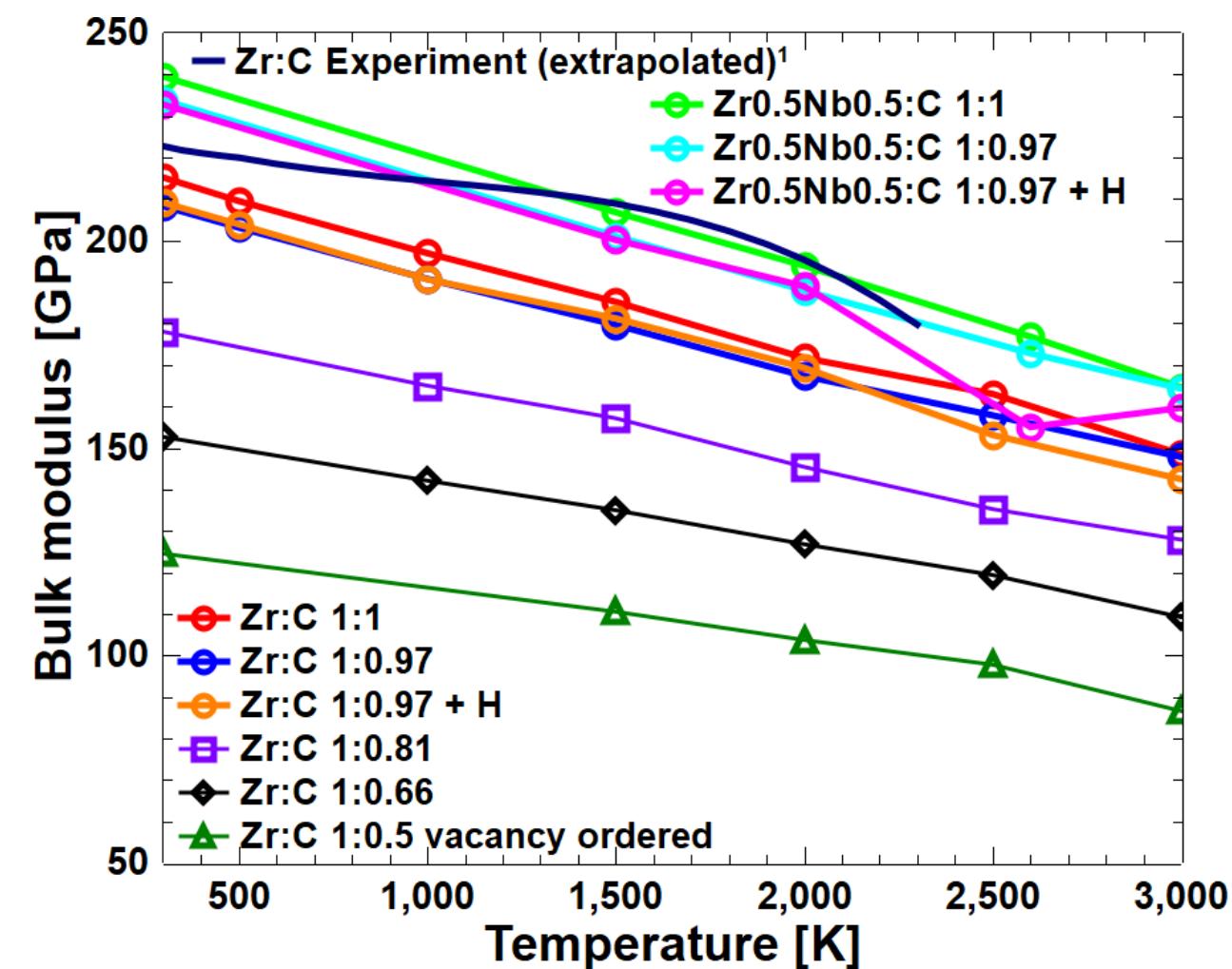
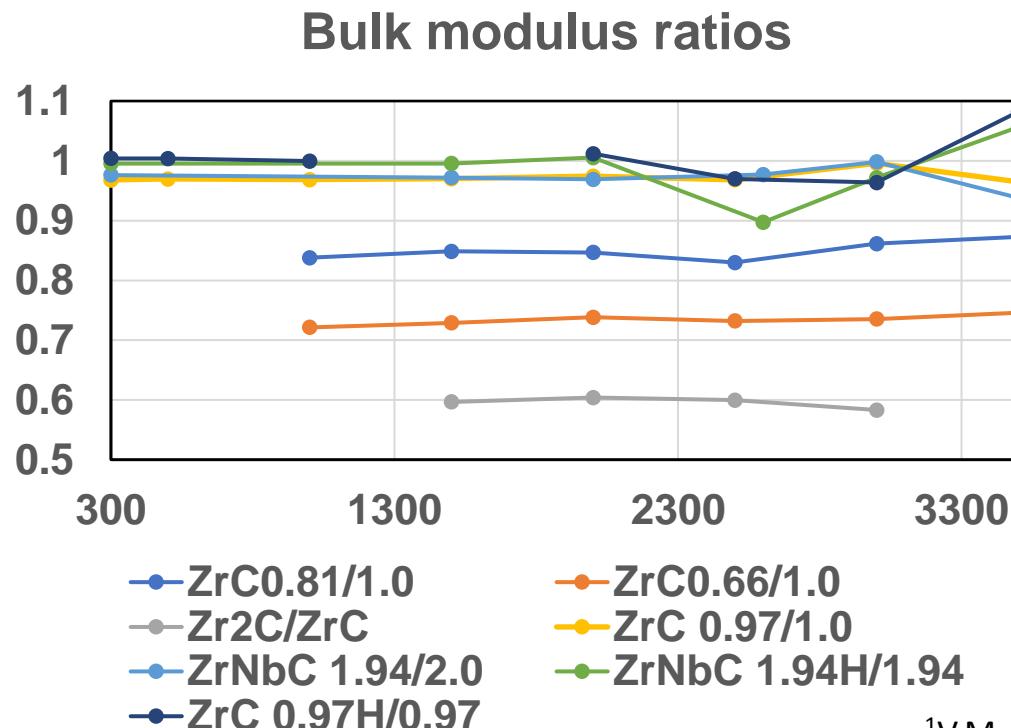


.. to ZrNb:C 1:1

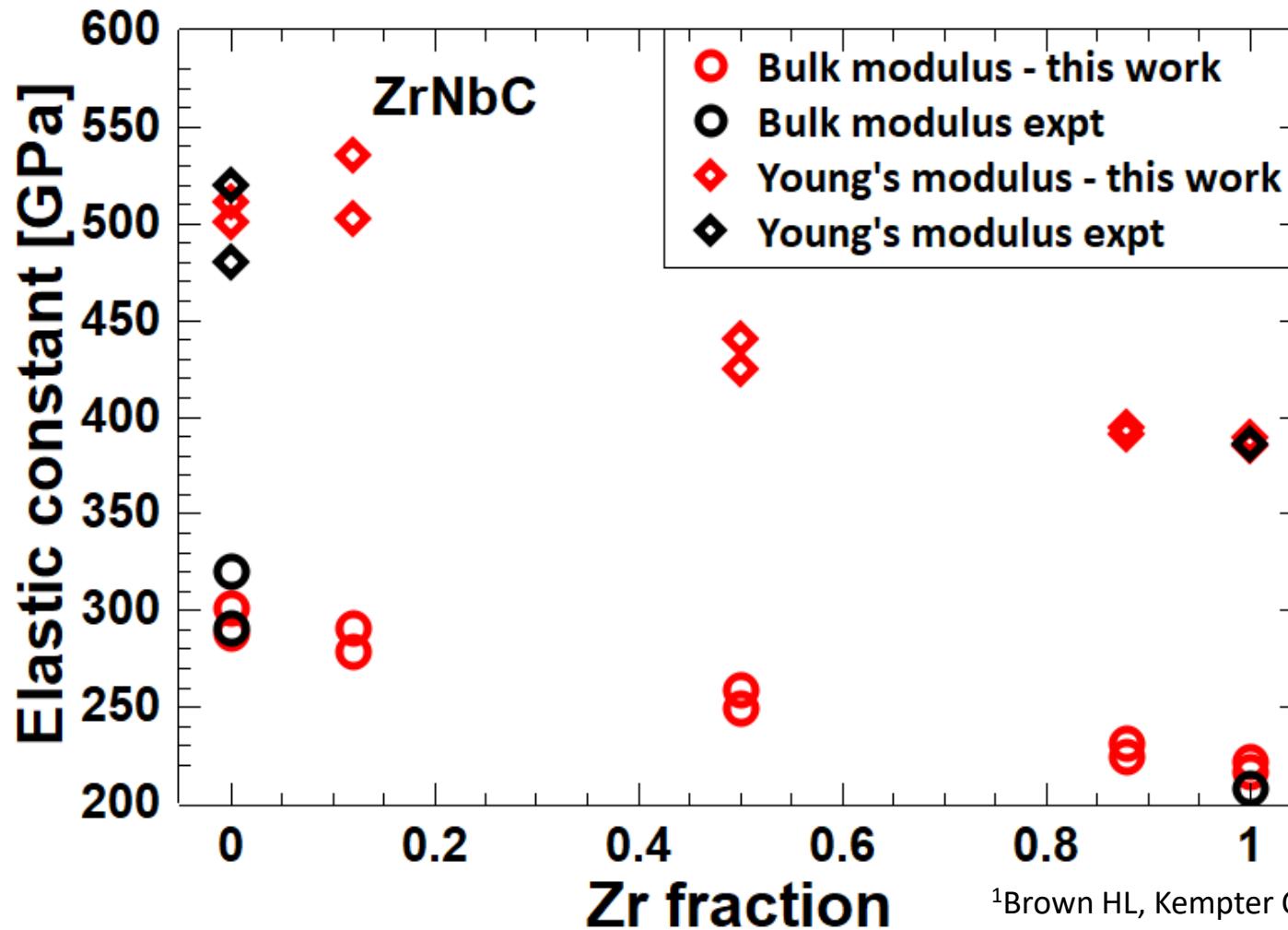


# Mechanical Properties - DFT

- High temperature bulk modulus:
  - Experimental slope compares favorably with a mixture of stoichiometries, their PR was a bit high
  - The presence of vacancies also leads to reduced elastic constants
  - H in vacancies softens both materials around 2500K



# ZrNbC Mechanical Properties - DFT



Material	Young E	Sigma	Pugh ratio
Zr1Nb0C0.97	385	0.203	1.35
Zr0.87Nb0.13C0.97	391	0.209	1.39
Zr0.5Nb0.5C0.97	425	0.214	1.42
Zr0.5Nb0.5C0.97H	427	0.211	1.41
Zr0.13Nb0.87C0.97	502	0.202	1.35
Nb0.5Ta0.5C0.97	506	0.217	1.43
Zr0.5Ta0.5C0.97	443	0.217	1.44

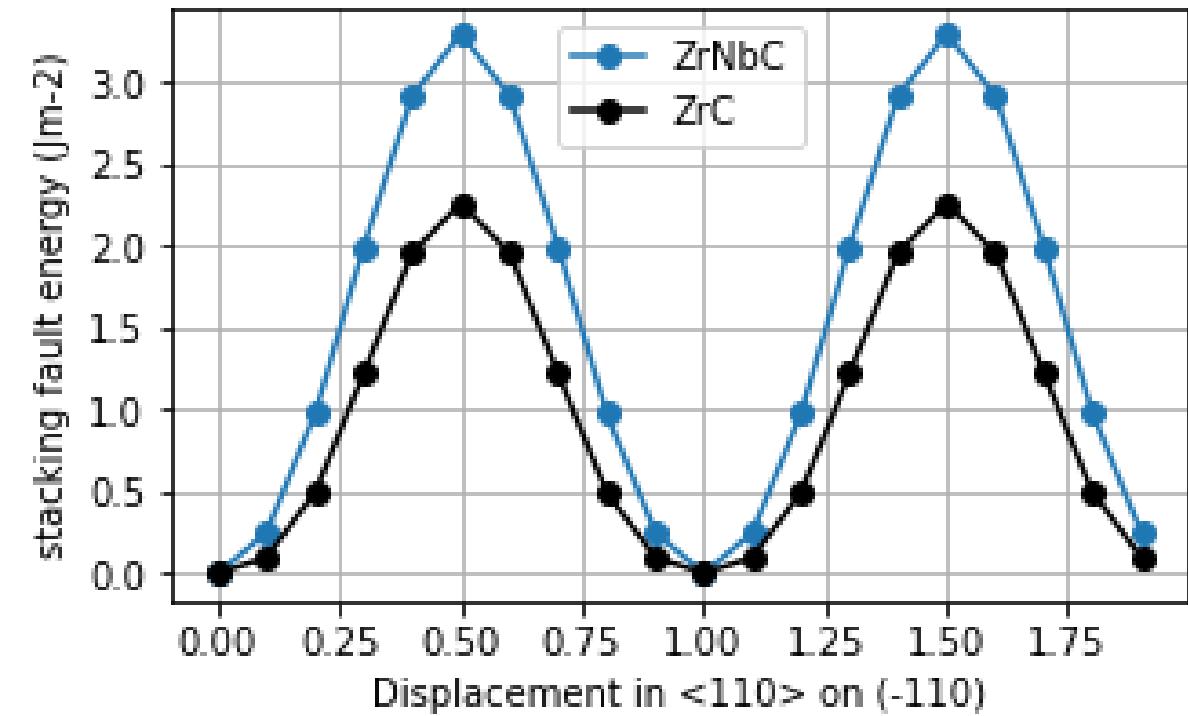
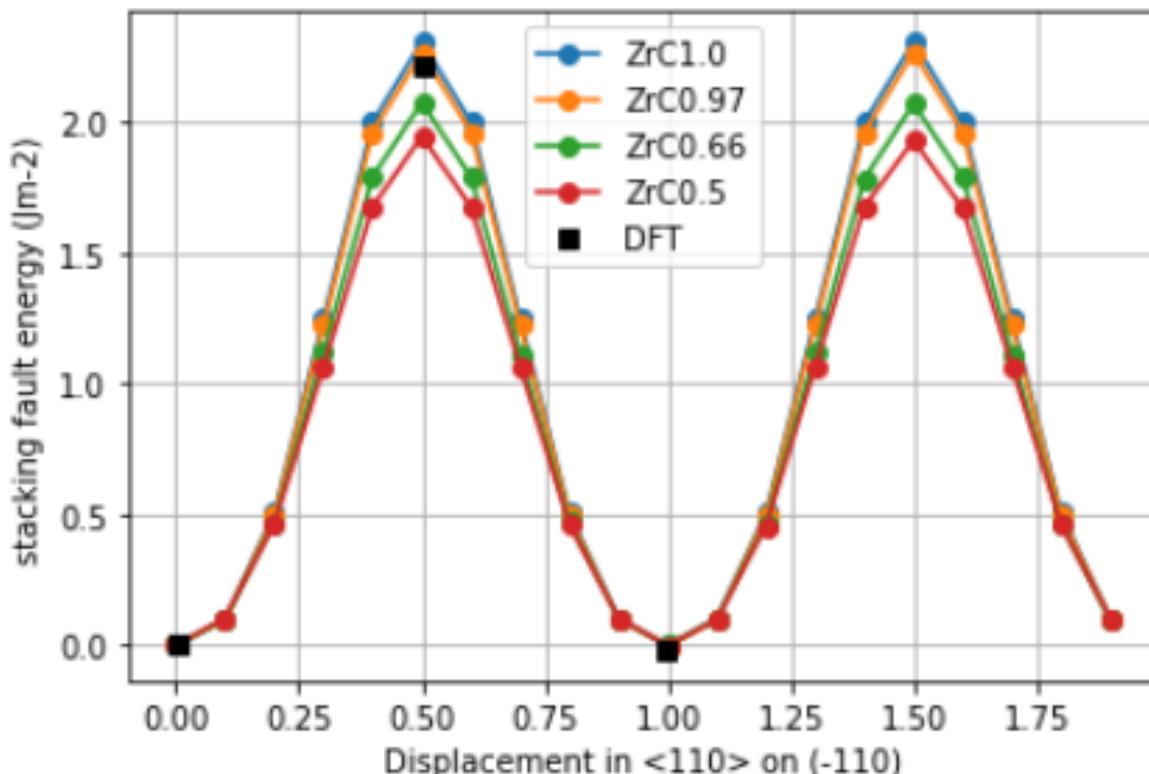
<sup>1</sup>Brown HL, Kempfer CP. Elastic properties of zirconium carbide. physica status solidi (b) 1966;18:K21–K23. doi: 10.1002/pssb.19660180150

<sup>2</sup>Cuppari MGDV, Santos SF. Physical Properties of the NbC Carbide. Metals. 2016; 6(10):250. <https://doi.org/10.3390/met6100250>

# MD for mechanical properties

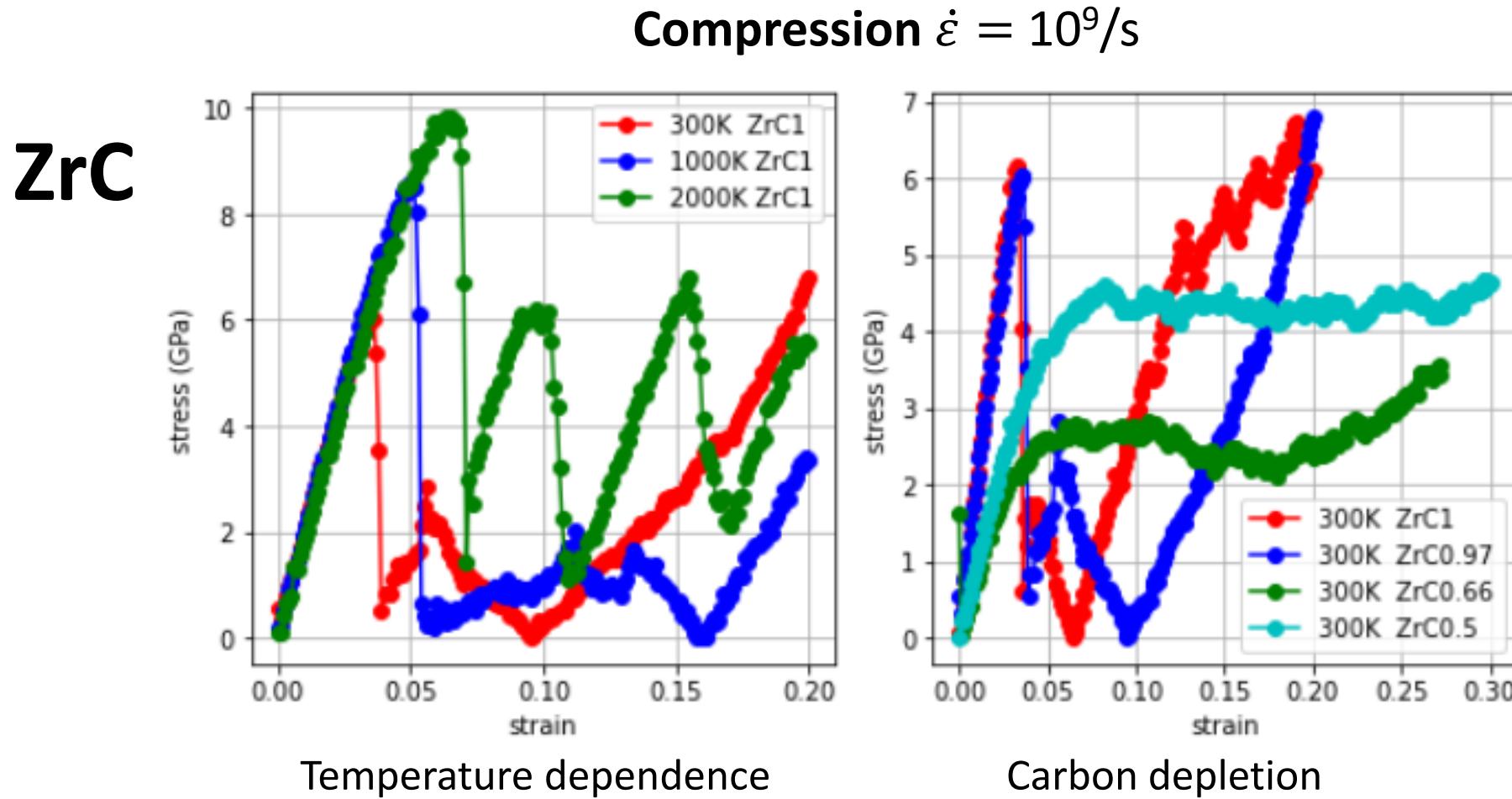


- **SNAP<sup>1</sup>** (Spectral Neighbor Analysis Potentials) developed at Sandia National Laboratories:
  - Geometric description using bispectrum
  - Energy (and force) fitting using linear regression



<sup>1</sup>Extending the accuracy of the SNAP interatomic potential form

# MD for mechanical properties



# Conclusions



Main findings:

- Calculations indicate ZrC is less likely to lose carbon than NbC or TaC – could explain heritage NERVA data on ZrC vs NbC mass loss performance
- Binary mixtures show compositions that are more stable than their end-member counterparts
- H diffusion in stoichiometric ZrC found to be slightly higher than previously theorized, but hydrogen saturation of carbon vacancies will hinder further hydrogen diffusion through the bulk. H diffusion in ZrNbC is slightly enhanced over ZrC.
- As carbon is depleted, deformation mechanism of ZrC changes from brittle to ductile

Remaining questions:

- Can mixing carbides prevent carbon loss?
- How quickly does coating carbon loss occur, and do we expect carbon/carbon loss from migration through the coating?
- How do vacancies and grain boundaries influence hydrogen migration through the coatings?
- How do vacancies and hydrogen influence the fracture toughness of (mixed) carbides?

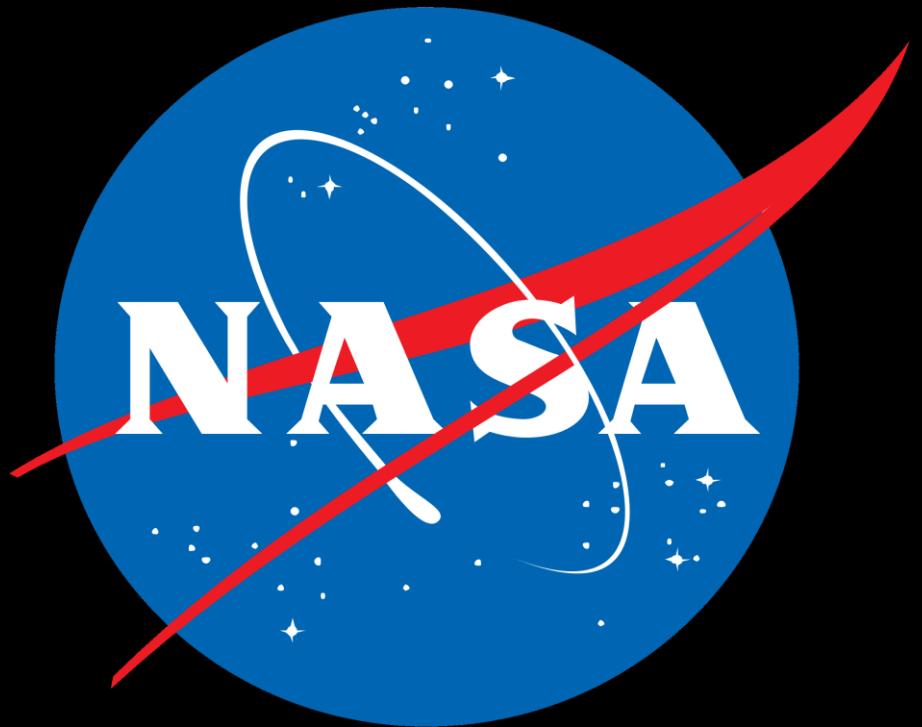


# Questions/comments?

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